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Evaluation of parameter uncertainties during the determination of the intrinsic viscosity of polymer solutions

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Abstract

In this work, it is shown that quadratic approximations of the function that relates the viscosity of polymer solutions with the polymer concentration lead to values of the intrinsic viscosity that are much more uncertain than the values obtained through simpler linear fits. Therefore, in spite of the expected better interpolations provided by second-order approximations, statistical arguments show that the use of linear fits is advisable when the number of experimental points available for the determination of intrinsic viscosities is small. Experimental data available for solutions of poly(4,4′-diphenylether-1,3,4-oxadiazole)s, POD-DPE, in sulfuric acid are used to illustrate this point. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The determination of the intrinsic viscosity of polymer solutions is a good alternative to monitor the variation of polymer average molecular weight during polymerization reactions. This is specially true for polymer resins that present poor solubility in the organic solvents that are frequently used for size exclusion chromatography (SEC) and light scattering measurements. The intrinsic viscosity can be related to the polymer average molecular weight through the well-known Mark–Houwink equation [1], as

$$[\eta] = K \times \bar{M}_{\mathrm{v}}^{a} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, K and a are parameters that depend on the solvent/polymer pair (assuming that additional thermodynamic states are kept constant), and $\bar{M}_{\mathrm{v}}$ is the viscosity-average molecular weight of the polymer. The intrinsic viscosity can be determined experimentally through measurements of the inherent and specific polymer viscosities, defined as

$$\eta_{\mathrm{inh}} = \frac{\ln(t/t_0)}{c} \tag{2}$$

$$\eta_{\mathrm{sp}} = \frac{t - t_0}{t_0} \tag{3}$$

where η_{inh} is the inherent polymer viscosity, η_{sp} is the specific polymer viscosity, t is the flow time of the polymer solution through a capillary tube of known diameter and length, t_0 is the flow time of the pure solvent through the same capillary tube and c is the concentration of the polymer solution (g/dl).

The inherent and specific viscosities are functions of the polymer concentration, usually described as series expansions in the form [2]

$$\eta_{\mathrm{inh}} = [\eta] + k_{\mathrm{inh}}[\eta]^2 c \tag{4}$$

$$\frac{\eta_{\mathrm{sp}}}{c} = [\eta] + k_{\mathrm{sp}}[\eta]^2 c \tag{5}$$

where k_{inh} and k_{sp} are constants that depend on the solvent/polymer pair.

The intrinsic viscosity is then usually determined as the limit of the inherent viscosity or of the ratio between the specific viscosity and the polymer concentration when the polymer concentration approaches zero.

$$[\eta] = \lim_{c \to 0} \eta_{\mathrm{inh}} = \lim_{c \to 0} \frac{\eta_{\mathrm{sp}}}{c} \tag{6}$$

From the point of view of parameter estimation, the determination of the intrinsic viscosity is similar to the estimation of the independent coefficients of Eqs. (4) and (5). As experimental points contain measurement errors, parameter estimates are also uncertain to a certain extent, which means that the estimated intrinsic viscosity is subject to

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fluctuations that must be evaluated, specially if it is used to monitor reaction conditions. It is also important to emphasize that variables measured experimentally are the polymer concentration and the flow time. The inherent and specific viscosities are obtained through manipulation of the measured experimental data and are not measured. Therefore, if least-squares is to be used for parameter estimation and curve fitting, it is advisable to write Eqs. (4) and (5) in terms of the originally measured experimental data [3]. For Eq. (5), for instance, it takes the form:

$$\frac{t - t_0}{t_0} = \eta_{\mathrm{sp}} = [\eta]c + k[\eta]^2 c^2 \tag{7}$$

where it may be assumed that the experimental errors are concentrated on the evaluation of the flow time of the polymer solution (due to fluctuations of polymer concentration, sampling of the polymer solution, fluctuations of measuring conditions—specially temperature—, etc.) and are essentially the same in all experimental conditions. Given this assumption, it may be said that the "measurement" errors of both the inherent viscosity and the ratio between the specific viscosity and the polymer concentration may vary very significantly from one experimental point to the other, so that the least-squares technique is not adequate to provide good parameter estimates for Eqs. (4) and (5).

For all the reasons given above, the intrinsic viscosity may be obtained as the linear parameter estimate (a) of the quadratic curve $\hat{y} = ax + bx^2$, where $\hat{y}$ is the specific viscosity and x is the polymer concentration. If experimental errors are concentrated on the measurement of $\hat{y}$, are constant throughout the experimental grid and are distributed normally, then using the least-squares estimation procedure [3]

$$a = \frac{\left(\sum_{i=1}^{n} y_i^{\mathrm{e}} x_i^{\mathrm{e}}\right)\left(\sum_{i=1}^{n} (x_i^{\mathrm{e}})^4\right) - \left(\sum_{i=1}^{n} y_i^{\mathrm{e}} (x_i^{\mathrm{e}})^2\right)\left(\sum_{i=1}^{n} (x_i^{\mathrm{e}})^3\right)}{\left(\sum_{i=1}^{n} (x_i^{\mathrm{e}})^4\right)\left(\sum_{i=1}^{n} (x_i^{\mathrm{e}})^2\right) - \left(\sum_{i=1}^{n} (x_i^{\mathrm{e}})^3\right)^2} \tag{8}$$

$$\sigma_a^2 = \frac{\sigma_y^2 \times \sum_{i=1}^{n} (x_i^{\mathrm{e}})^4}{\left(\sum_{i=1}^{n} (x_i^{\mathrm{e}})^4\right)\left(\sum_{i=1}^{n} (x_i^{\mathrm{e}})^2\right) - \left(\sum_{i=1}^{n} (x_i^{\mathrm{e}})^3\right)^2} \tag{9}$$

$$\sigma_{[\eta]}^2 = \sigma_a^2 \tag{10}$$

where x_i^{e} and y_i^{e} are the experimental values for polymer concentrations and specific viscosity, respectively, and σ_a^2 and σ_y^2 are the variances involved on the determination of the parameter a and of the experimental value of the specific viscosity.

Choosing typical values of polymer concentrations (x_i^{e}) used for the preparation of the polymer solutions, such as 0.1, 0.3 and 0.5 g/dl, then

$$\sigma_{[\eta]}^2 \cong 53\sigma_y^2 \tag{11}$$

so that the determination of the intrinsic viscosity may present significant errors.

Given the low polymer concentrations, one may wonder whether the second-order terms are needed for the series expansions presented in Eqs. (4) and (5). If the series expansion is truncated after the linear term, following the same arguments presented before, then

$$\eta_{\mathrm{sp}} = [\eta]_{\mathrm{lin}} c \tag{12}$$

which means that the intrinsic viscosity may be defined as the initial angular coefficient of the curve that represents how η_{sp} depends on the polymer concentration. In the following paragraphs, the intrinsic viscosity computed from Eq. (7) is represented by $[\eta]$, while the intrinsic viscosity computed from Eq. (12) is represented by $[\eta]_{\mathrm{lin}}$. If the least-squares procedure is used to provide an estimate of $[\eta]_{\mathrm{lin}}$, using the equation $\hat{y} = ax$, then

$$a = \frac{\sum_{i=1}^{n} y_i^{\mathrm{e}} x_i^{\mathrm{e}}}{\sum_{i=1}^{n} (x_i^{\mathrm{e}})^2} \tag{13}$$

Table 1
Reaction conditions for the preparation of the polymer samples

Sample[a]	t (h)	T (°C)	PPA/HS[b]	HS/DPE[b]
1	7	160	20	1.2
2	7	160	10	0.8
3	7	100	20	0.8
4	7	100	10	1.2
5	3	160	20	0.8
6	3	160	10	1.2
7	3	100	20	1.2
8	3	100	10	0.8
9	5	130	15	1.0
10	5	130	15	1.0
11	5	130	15	1.0
12	5	130	15	1.0
13	4	150	18	1.0
14	1	150	18	1.0
15	7	160	20	1.2
16	7	160	10	0.8
17	3	160	10	1.2
18	7	160	20	0.8
19	7	160	10	1.2
20	3	160	20	1.2
21	3	160	10	0.8
22	5	160	15	1.0
23	5	130	15	1.2

[a] Samples obtained through solution polymerization of phenylenedicarboxylic acid (DPE) and hydrazine sulfate (HS) in poly(phosphoric acid) (PPA).

[b] Molar feed ratio.

Table 2
Specific viscosities and average molecular weight obtained for polymer samples

Sample	c_1 (g/dl)	$[\eta]_{\mathrm{sp1}}$	c_2 (g/dl)	$[\eta]_{\mathrm{sp2}}$	c_3 (g/dl)	$[\eta]_{\mathrm{sp3}}$	$\bar{M}_{\mathrm{w}}$ [a] (kDa)
1	0.1170	0.0164	0.2390	0.0415	0.4690	0.1113	33
2	0.1300	0.0408	0.3012	0.0886	0.4969	0.1432	47
3	0.1928	0.1701	0.2588	0.2349	0.5072	0.5237	–
4	0.1219	0.0391	0.2618	0.0787	0.4883	0.1380	–
5	0.1229	0.0447	0.2353	0.1114	0.4977	0.2700	–
6	0.1396	0.0989	0.4232	0.3273	0.5581	0.4524	129
7	0.1689	0.0481	0.2164	0.0722	0.5043	0.1070	–
8	0.1153	0.0332	0.2523	0.0759	0.5024	0.1373	–
9	0.1753	0.1434	0.2166	0.1684	0.5075	0.3959	–
10	0.1545	0.1630	0.2355	0.2456	0.4939	0.5578	–
11	0.1535	0.1608	0.2522	0.2742	0.4814	0.5823	–
12	0.1595	0.1065	0.2695	0.1935	0.4779	0.3752	–
13	0.1619	0.0426	0.3039	0.0941	0.5112	0.1788	38
14	0.1883	0.0046	0.2063	0.0061	0.4561	0.0218	–
15	0.1624	0.0348	0.2541	0.0612	0.5053	0.1635	54
16	0.1335	0.0647	0.2615	0.1588	0.5225	0.3080	94
17	0.1287	0.1233	0.2949	0.2972	0.5364	0.5845	138
18	0.1601	0.1562	0.2585	0.2338	0.4892	0.3503	128
19	0.1703	0.0907	0.2862	0.1425	0.5520	0.2228	81
20	0.1647	0.0133	0.2667	0.0166	0.5989	0.0612	17
21	0.1360	0.0179	0.2809	0.0458	0.5036	0.0580	26
22	0.1898	0.0378	0.2741	0.0747	0.4366	0.1045	30
23	0.1592	0.0575	0.2719	0.0804	0.5054	0.2119	50

[a] Measured by SEC, using NMP as solvent.

$$\sigma_a^2 = \frac{\sigma_y^2}{\sum_{i=1}^{n} (x_i^{\mathrm{e}})^2} \tag{14}$$

$$\sigma_{[\eta]_{\mathrm{lin}}}^2 = \sigma_a^2 \tag{15}$$

Using the same typical values of polymer concentrations presented before, then

$$\sigma_{[\eta]_{\mathrm{lin}}}^2 \cong 3\sigma_y^2 \tag{16}$$

which means that uncertainties are significantly lower than in the previous case. Therefore it seems that there may be no reason to use the second-order expansion to estimate the intrinsic viscosity of a certain polymer solution. This approach is demonstrated experimentally in next paragraphs using polyoxadiazole as a model polymer.

2. Experimental

Poly(1,3,4-oxadiazole)s [4,5] are among the polymers that present poor solubility in common organic solvents. These polymers are being used for the preparation of polymer membranes for gas separation. Given the physical properties of this family of polymers, the intrinsic viscosity, or even the specific viscosity evaluated at a certain concentration, is often used to determine the polymer average molecular weight [6–8]. For this reason, polymer samples of POD-DPE prepared at different reaction conditions [9] were characterized through viscometry and SEC measurements,

Table 3
Inherent viscosities and model correlations for polymer samples

Sample	$[\eta]_{\mathrm{lin}}$ [a] (dl/g)	R^2 [b]	$[\eta]$ [a] (dl/g)	R^2 [c]
1	0.22	0.98	0.13	0.99
2	0.29	1.00	0.32	0.94
3	0.99	1.00	0.80	0.97
4	0.29	1.00	0.33	0.98
5	0.52	0.99	0.34	0.83
6	0.79	1.00	0.68	0.93
7	0.24	0.97	0.36	0.81
8	0.28	1.00	0.29	0.89
9	0.78	1.00	0.79	0.89
10	1.11	1.00	0.99	0.88
11	1.17	1.00	0.98	0.91
12	0.76	1.00	0.62	0.87
13	0.33	0.99	0.23	0.95
14	0.04	0.95	0.01	0.97
15	0.30	0.98	0.17	1.00
16	0.59	1.00	0.49	0.09
17	1.07	1.00	0.92	1.00
18	0.77	0.99	1.05	1.00
19	0.43	0.99	0.57	1.00
20	0.10	0.98	0.06	0.55
21	0.13	0.99	0.15	0.26
22	0.24	0.99	0.20	0.10
23	0.39	0.98	0.30	0.23

[a] Measured in an Ostwald type viscometer ($D_{\mathrm{I}} = 1.27$ mm) in sulfuric acid at 30°C.

[b] Correlation coefficient of the curve η_{sp} as a function of polymer concentration.

[c] Correlation coefficient of the curve η_{sp}/c as a function of polymer concentration.

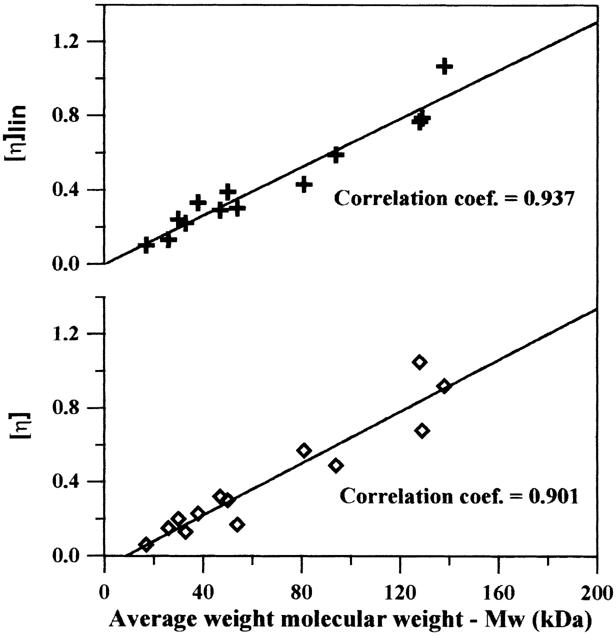

Fig. 1. Correlation of $[\eta]$ and $[\eta]_{\rm lin}$ as a functions of $\bar{M}_{\rm w}$.

in order to allow the determination of the polymer-average molecular weight. The detailed description of the experimental procedures is presented elsewhere [9] and is beyond the scope of this note. It is important to say, though, that specific viscosities were measured in solutions of sulfuric acid and that SEC measurements were carried out in solutions of *N*-methyl-2-pyrrolidone (NMP). As some POD-DPE samples are not soluble in NMP, some SEC measurements are not available.

3. Results and discussion

Table 1 presents the reaction conditions used to prepare the POD-DPE samples. Table 2 presents the values obtained for the specific viscosity for each polymer sample at different polymer concentrations and the polymer-average molecular weight obtained through SEC, when available. Table 3 presents the values obtained for the intrinsic viscosity using both estimation procedures and the final correlations of the model fits for Eqs. (12) and (5). It can be observed that the correlation coefficients obtained for the determination of $[\eta]_{\rm lin}$ is usually much higher than in the other case, despite the smaller number of parameters. This result may be used to support the previous assumptions regarding the larger experimental errors involved when the second order expansion is used to allow the estimation of the intrinsic viscosity.

Fig. 1 presents the correlations for $[\eta]$ and $[\eta]_{\rm lin}$ as functions of the polymer weight-average molecular weight, $\bar{M}_{\rm w}$, obtained by SEC. Although the intrinsic viscosity is related to $\bar{M}_{\rm v}$, in most cases $\bar{M}_{\rm v}$ is a multiple of $\bar{M}_{\rm w}$, so that $\bar{M}_{\rm v}$ can usually be replaced by $\bar{M}_{\rm w}$ in Eq. (1). As shown in Fig. 1, $[\eta]_{\rm lin}$ presents a very good correlation with $\bar{M}_{\rm w}$, presenting higher correlation coefficients than those obtained for $[\eta]$, showing that $[\eta]_{\rm lin}$ provides a very good evaluation of $\bar{M}_{\rm w}$.

4. Conclusions

The computation of the intrinsic viscosity of polymer solutions as the angular coefficient of a simple linear fit of the specific viscosity as a function of polymer concentration leads to much better results than the usual procedure, which computes the intrinsic viscosity as the linear coefficient of the second-order approximation of the function which relates the specific viscosity and the polymer concentration. This was shown to be mainly due to the much higher uncertainties of the final parameter estimates observed when the second procedure is used. The results obtained experimentally with POD-DPE samples confirm the theoretical expectations and show that the simple linear fits lead to very good description of polymer-average molecular weight, allowing a robust description of polymerization conditions.

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